

COATINGS

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COATINGS BASED ON PHOSPHATE BINDERS

V. I. Vereshchagin,¹ Vas. V. Guzeev,¹ Vit. V. Guzeev¹Translated from *Steklo i Keramika*, No. 6, pp. 28–29, June, 2000.

Hydroxyapatite coatings based on phosphate binders are described. Their adhesion characteristics, the TCLE, and the effect of the temperature on the strength of the material of the coatings are presented. Coatings based on phosphate binders can present interest for specialists in electrochemistry and medicine.

A special place among inorganic binders belongs to phosphate binders used as components of building materials, refractories, adhesives, and asphalt-concretes [1]. One of the main properties of ceramic materials obtained with the use of phosphate binders is the ability to form strong structures under a relatively low temperature and preserve its strength characteristics upon heating [2].

The necessity to prolong the service life of equipment and the growing demand for decorative and corrosion-resistant coats requires the creation of new protective materials capable of preserving their properties under the action of the atmosphere and aggressive media. Such materials are often based on phosphate binders [1].

In some electrochemical processes the electrode can bear other phases in addition to the conductor of electrons, for example, solid reagents, additives, and protective coatings that increase the service life and improve the service properties of the electrode [3].

The present study is devoted to materials based on phosphate binders and their use as protective coatings of conducting materials produced from titanium alloys and serving as apparatuses for cleaning aqueous solutions, i.e., electrocoagulators working in media with pH ranging from 3 to 12. The presence of Ca^{2+} ions and $(\text{PO}_4)^{3-}$ phosphate groups in the composition of the coating determined our choice of the powder filler. If we take into account some special features of the technology of phosphate coatings where an overly active interaction between salts containing Ca^{2+} ions and phosphoric acid is concerned, we will see that the choice of the mixing liquid and the powder filler plays an important role. We narrowed our choice to alumophosphate binders and hydroxyapatite (HA) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ obtained by roasting bone meal. An x-ray phase analysis has shown (see Table 1)

that the studied powder bears whitlockite $[\text{Ca}_3(\text{PO}_4)_2]$ and brushite $(\text{CaHPO}_4 \cdot 2\text{H}_2\text{O})$ phases and an unidentified crystalline phase in addition to the hydroxyapatite.

The hydroxyapatite did not interact actively with the alumophosphate binders and the setting time turned out to be sufficient for depositing the slip onto the substrate.

The ready product obtained by the slip technology contains (in accordance with the stoichiometric calculation) the following components: 57.75–78.06% phosphorus (as recalculated for P_2O_5), 0.77–0.90% H_2O , 17.06–19.87% calcium (as recalculated for CaO), and 0–11.86% aluminum (as recalculated for Al_2O_3).

The slip method for deposition of the HA powder on the metallic substrate is widely used in medicine for obtaining coatings, but the high temperature of roasting (900–1000°C)

TABLE 1

Peak	Parameters of specimen		Identified phase
	$d, \text{\AA}$	Int, %	
1	8.161	10	—
2	4.069	5	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$
3	3.443	28	The same
4	3.178	8	"
5	3.079	18	"
6	2.810	100	"
7	2.785	46	"
8	2.714	73	$\text{Ca}_3(\text{PO}_4)_2$
9	2.637	26	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$
10	2.261	25	The same
11	2.151	7	"
12	1.943	30	"
13	1.892	15	"
14	1.869	6	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

¹ Tomsk Polytechnical University, Tomsk, Russia.

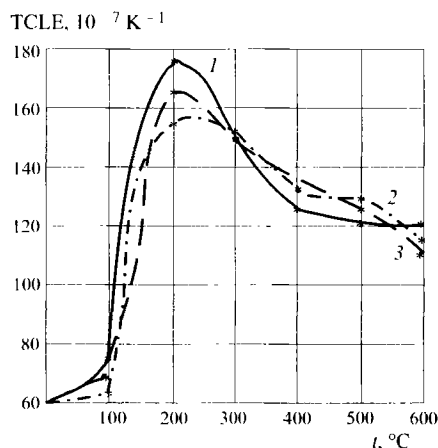


Fig. 1. TCLE of specimens as a function of the temperature at a HA/alumophosphate binder proportion of 0.75 (1), 0.80 (2), and 0.90 (3).

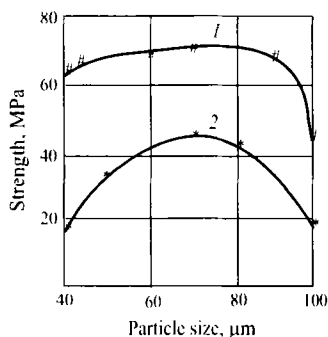


Fig. 2. Dependence of the compressive strength of specimens on the granulometric composition at a roasting temperature of 300°C (1) and 600°C (2).

[4] causes rejects because of the poor correspondence between the TCLE and the possibility of scale formation on the surface of the metallic substrate.

We studied the TCLE of the obtained coatings as a function of the temperature and the content of the components which was changed by varying the proportion of the HA powder and the alumophosphate binder in making slip. The results of the measurements are presented in Fig. 1.

The studies were performed by the dilatometric method at a mean heating rate of 3–5 K/min. The alumophosphate binder was AFS-3 fabricated by the method described in [1].

It can be seen from Fig. 1 that the change in the HA/binder proportion does not affect much the TCLE of the material, but the use of compositions with a high binder content has a favorable effect on the technology of deposition of the coating and decreases the probability of rejection after the heat treatment due to the elastic properties of the phosphate material [1].

The values of the TCLE of the obtained coatings are comparable with the TCLE of metallic materials, i.e., $(7-15) \times 10^{-6} \text{ K}^{-1}$. However, it should be noted that the

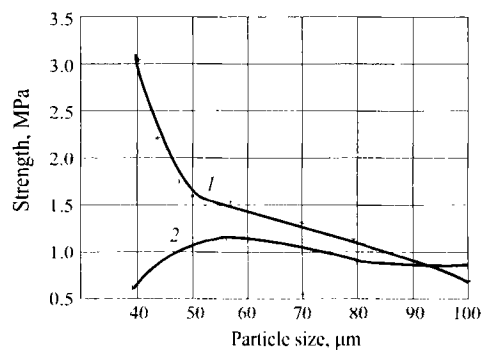


Fig. 3. Strength of cohesion between the coating and the substrate upon shear: 1) smooth surface; 2) porous surface.

heating rate in the heat treatment should not be too high, because the phosphate groups are strongly bound to the water molecules, which can be a cause of bloats on the parts or breaking-off of the coating [1].

In order to determine the strength characteristics of the material we fabricated specimens by the method of semidry pressing of hydroxyapatite powder with a phosphate binder. The HA powder was separated into fractions (from <40 to 100 μm). Then we studied the effect of the granulometric composition of the HA powder and the roasting temperature on the strength characteristics of the materials (Fig. 2). It can be seen that the specimens fabricated from the powder with particle size of 71–80 μm possess a higher strength, which can be explained by the maximum density of particle packing in the case of fine disperse fractions.

The compression strength of specimens with a roasting temperature exceeding 300°C is higher than that of specimens with a final roasting temperature of 600°C. The authors of [5] associate this with the restructuring of phosphate groups, which begins at a temperature of 600°C and ends at 1000°C, and is accompanied by breaking of the polymer phosphate chains, which diminishes the strength.

When depositing a coating we should know the adhesion of the material, i.e., perform shear or rupture tests. We determined the dependence of the strength of cohesion between the material and the substrate upon shear on the granulometric composition of the specimens obtained after heat treatment at 350°C (Fig. 3). The coatings were deposited onto the specimens with a smooth and porous surface. The highest adhesion was exhibited by specimens with a coating deposited onto a smooth surface. The maximum strength in the shear tests was 3.03 MPa, which corresponds to the strength of a material obtained from a powder with particles less than 40 μm in size. A porous surface has a smaller useful area, which explains the total decrease in the strength upon shear.

The studied coatings possessed a good resistance to neutral acid and weakly alkaline media when tested under the conditions of electrochemical processes. After a one-month service at $\text{pH} = 3-12$ at a current density of 5–8 kA/m^2 we did not detect a decrease in the mass. It should be noted that

hydroxyapatite is a bioactive material and can be used for coating metallic endoprostheses in the case of positive reaction of human tissue to the material of the coating [6].

Thus, coatings based on alumophosphate binders can present interest for specialists in electrochemistry and medicine. The obtained materials can be used as electroprotective coatings for electrodes (electrocoagulators, electrolyzers) or as coatings of endoprostheses used in reconstructive surgery of the osteal-articular system of man.

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